Electrochemically Induced Surface Dimerization in SWV-MATHCAD

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$EsI := 0.3 \quad \Delta E := 0.8 \quad dE := 0.004 \quad Esw := 0.085$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad \alpha := 0.5$

$ks := 2.5 \quad kf := 0.0005 \quad cOx := 10.0 \quad rs := 1$

$f := 10 \quad kb := 0.0005 \quad cs := \frac{cOx}{rs}$

$Ket := \frac{ks}{f} \quad Keq := 1.00$

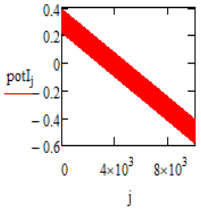
MATHCAD FILE

ELECTROCHEMICALLY INDUCED DIMERIZATION IN LIPOPHILIC REDOX PROTEINS
THEORETICAL INSIGHTS IN SQUARE-WAVE VOLTAMMETRY

$j := 1..\frac{\Delta E}{dE} \cdot 50$

$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

$$Kchem := \frac{(kf + kb)}{f}$$



$$M_j := e^{-Kchem\cdot\frac{j}{50}} - e^{-Kchem\cdot\frac{j+1}{50}}$$

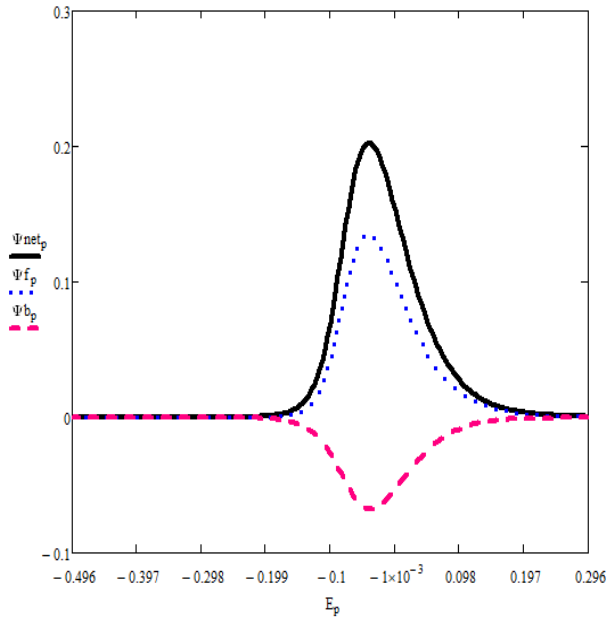
$$\Phi I_j := n\cdot\frac{F}{1R\cdot T}\cdot potI_j$$

$$\Psi I_1 := \frac{Ket\cdot e^{-\alpha\cdot\Phi I_1}}{1 + \frac{Ket}{50}\cdot e^{-\alpha\cdot\Phi I_1} + \frac{1}{cs}\,Ket\,Kchem^{-1}\cdot e^{\Phi I_1\cdot(1-\alpha)}\cdot M_1}$$

$$\Psi I_j := \frac{\frac{Ket}{cs}\cdot e^{-\alpha\cdot\Phi I_j} - \frac{Ket}{50\cdot cs}\cdot e^{-\alpha\cdot\Phi I_j}\cdot\sum_{i=1}^{j-1}\Psi I_i - \left(\frac{1}{1}\right)\cdot\left[1\,\frac{Ket}{1}\,Kchem^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha)}\cdot\sum_{i=1}^{j-1}\left(\Psi I_i\cdot M_j\right) - \frac{1Keq}{1+Keq}\,Kchem^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha)}\cdot\sum_{i=1}^{j-1}\left(\Psi I_i\cdot M_j\right)\right]^2}{1 + \frac{Ket}{50\cdot cs}\cdot e^{-\alpha\cdot\Phi I_j} + \frac{1}{1}\,1\left[1\,\frac{Ket}{1}\,Kchem^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha)}\cdot M_1 - \frac{1Keq}{1+Keq}\,Kchem^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha)}\cdot M_1\right]^2}$$

$\Psi_j := \Psi I_j \qquad p := 1..\left(\frac{\Delta E}{dE}\right) - 1$

$\Psi b_p := \Psi_{50\cdot p+25} \qquad \Psi f_p := \Psi_{(p+1)\cdot 50} \qquad \Psi net_p := \Psi f_p - \Psi b_p \qquad E_p := EsI - p\cdot dE$



Surface E-dimerization mechanism in SWV
Ox(ads) + 1e- = Red(ads)
2Red(ads)<---> D

Meaning of symbols in the MATHCAD File

ks is standard rate constant of electron rtansfer (s-1)
kf is forward rate constant of dimerization step
kb is reverse rate constant of dimerization step
f is the SW frequency (Hz)
Esw is SW amplitude (V)
dE is potential step (V)
n is number of electrons exchanged
α is electron transfer coefficient
F is Farady constant
R is universal gas constant
T is thermodynamic temperature
cOx is molar concentration of Ox
rs is auxilary constant
cs is dimensionless concentration parameter
Kchem is chemical rate parameter of dimerization reaction
Keq is equilibrium constant of dimerization reaction
Mj is numerical integration factor
ΦIj is dimensionless potential
EsI is starting potential
Ket is dimensionless parameter related to electron transfer step
Ψ is symbol of the dimensionless current

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